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(54) PREPARATION OF CATHODE MATERIAL FOR LITHIUM BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a cathode material having low reactivity with an electrolytic solution and an excellent electric discharge characteristic by adding an org. solvent to a separated carbon core material and washing/drying and calcining after immersing the carbon core material in a carbon material for coating film formation.

SOLUTION: Washing of a carbon core material with an org. solvent is preferably carried out at 10-300°C after immersing the carbon core material in a coating film forming carbon material at 10-300°C. The coating film forming carbon material is a coal and/or petroleum heavy oil suitably a tar and/or a pitch which is preferably made to have primary QI of $\leq 3\%$ by removing previously at least a part of the primary QI. The org. solvent for washing is selected from toluene, quinoline, acetone or the like, a coal oil and a petroleum oil. Coating ratio (c) of the coating film forming carbon material/(core material + the coating film forming material) is preferably $0 < c \leq 0.3$. Spherical particles of which the

corner becomes round are obtained without pulverizing because inter particle fusion and aggregation do not occur even if carrying out washingdrying and calcining.

CLAIMS

[Claim(s)]

[Claim 1]A manufacturing method of a coating carbon material which has an enveloping layer on the surface adding and washing an organic solvent to a separated core material carbon materialand drying and calcinating it to it after a core material carbon material is immersed in a carbon material for covering formation.

[Claim 2]A manufacturing method of a carbon material which has an enveloping layer on the surface adding and washing an organic solvent to a separated core material carbon materialand drying and calcinating it to it after a core material carbon material is immersed in a carbon material for covering formation at 10-300 **.

[Claim 3]A manufacturing method of the coating carbon material according to claim 1 or 2 which adds an organic solvent to a separated core material carbon materialand is washed at 10-300 **.

[Claim 4]A manufacturing method of the coating carbon material according to any one of claims 1 to 3 which immerses in a carbon material for covering formation under decompression of a core material carbon material.

[Claim 5]A manufacturing method of the coating carbon material according to any one of claims 1 to 4 whose carbon materials for covering formation are a Carboniferous system and/or petroleum system heavy oil.

[Claim 6]A manufacturing method of the coating carbon material according to any one of claims 1 to 5 whose carbon materials for covering formation are tar and/or a pitch.

[Claim 7]A manufacturing method of the coating carbon material according to any one of claims 1 to 6 whose organic solvent used for washing is at least one sort chosen from toluenequinolineacetonehexanebenzenexylenemethylnaphthalenecolohsa Carboniferous system oiland a petroleum system oil.

[Claim 8]A manufacturing method of the coating carbon material according to any one of claims 1 to 7 a range of whose rate of solid content at the time of washing and an organic solvent is 1:0.1-10 in a weight ratio.

[Claim 9]A manufacturing method of the coating carbon material according to any one of claims 1 to 8 whose covering ratio (c) defined as a weight ratio of carbon material/for covering formation (carbon material for core material + covering formation) is $0 < c \leq 0.3$.

[Claim 10]A manufacturing method of the coating carbon material according to any one of claims 1 to 9 in which a carbon material for covering formation removes at least a part of primary QI beforehandand makes primary QI 3% or less.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

Work A carbon materials manufacturing methodespecially the surface more way part Nomoto invention about the end of carbon powder it was covered with ingredientssuch as

heavy oil and its manufacturing method in details. An isotropic graphite material raw material lithium secondary battery negative pole material etc. are carried out and it is related with a useful carbon material manufacturing method for the same and the lithium secondary battery using such a carbon material.

[0001] Back View A miniaturization and weight saving of portable equipments (henceforth a "portable device") such as an electronic device and information machines and equipment are advancing splendidly and the rechargeable battery which drives them is becoming very important parts in recent years [technical]. Since a lithium secondary battery has a light weight and high energy density promising ** is carried out as a power supply for a drive of a portable device and research and development are furthered actively. However when a lithium metal is used for an anode in order that a dendrite may generate and grow and may cause an internal short circuit on metal lithium by repeating a charging and discharging cycle rechargeable battery-izing is difficult. Although it replaces with a lithium metal and use of a lithium alloy like a lithium aluminum alloy is proposed if a charging and discharging cycle or deep charge and discharge is performed in this case in order that the segregation of an alloy etc. may start characteristic sufficient in the long run is not obtained.

[0002] Then a carbon material is used as a host material the cell using the anode using the insertion elimination reaction of the lithium ion is proposed and research and development have been furthered and put in practical use. The lithium secondary battery which uses a carbon material for an anode is excellent in a cycle characteristics safety etc.

[0003] However while a carbon material has a broad structure thru/or form of black lead to amorphous carbon in order that the fine texture which those property values or a carbonaceous hex-stee side forms may influence the performance of an electrode greatly various carbon materials which specified a property value or fine texture are proposed.

[0004] The thing of a carbon system which roughly divided and was calcinated at around 1000 ** and the thing of a black lead system calcinated at around 2800 ** are among the negative pole materials for lithium secondary batteries used now. The former has the advantage that there are few reactions with an electrolysis solution and disassembly of an electrolysis solution cannot break out easily when it uses as an anode of a lithium secondary battery but there is a fault that change of the potential accompanying discharge of a lithium ion is large. On the other hand the latter has the advantage that change of the potential accompanying discharge of a lithium ion is small when it uses as an anode of a lithium secondary battery but. It reacts to an electrolysis solution and disassembly of an electrolysis solution arises and there is a fault that a carbon material is destroyed further (J. Electrochem. Soc. 117222 (1970)). As a result in the latter problem such as decline in charge and discharge efficiency a fall of a cycle characteristic and a safety fall of a cell arise. Since it is reported that the material of a black lead system is also usable when using a specific electrolysis solution but (J. Electrochem. Soc. 1372009 (1990)) an electrolysis solution is limited when a cell is produced there is a problem that the improvement of the temperature characteristics of a cell a cycle characteristic etc. is considerably restricted by the kind of electrolysis solution.

[0005] JPH4-368778 A JPH4-370662 A JPH5-94838 A JPH5-121066 A etc. have proposed the carbon material which covered the graphite-grains child's surface with low crystal carbon that this problem should be solved. Since these surface treatment carbon materials press

down disassembly of an electrolysis solution they are effective to the increase in cell capacity and improvement of a cycle characteristic etc.

[0006] However, according to technology given in JPH4-368778A, since the carbon coating layer is formed in the carbon particle surface by the gaseous phase method, weld of each carbon particle, condensation etc., do not take place, but the material which was excellent in the performance is obtained, but it is field such as a cost aspect and mass production nature and there is a practically big problem.

[0007] The technique of having used promising liquid phase carbonization for JPH4-370662A, JPH5-94838A and JPH5-121066A from a cost aspect and mass production nature is indicated. However, by only mixing and calcinating the organic compound and graphite grains, child of the liquid phase. Since graphite grains, children weld and condense in the case of carbonization, problems like that an impurity mixes at the time of grinding which needs to grind material and a field [activity / black lead] newly exposes by grinding in the case of electrode production and a process becomes still more complicated are produced.

[0008] ** In indication this invention, the anode which there are not selectivity about an electrolysis solution thru/or restrictions and uses a carbon material with a small electrical change of discharge of a lithium ion is produced.

Therefore, it primarily aims to obtain the lithium secondary battery excellent in various characteristics such as cycle nature and safety.

[0009] The result of having inquired wholeheartedly this invention person canceling thru/or reducing the problem of the above conventional technologies, The particle state carbon material (there is also only the following "core material carbon material" thru/or "carbon material used as a core material" or "core material") used as a core material. The raw material for carbon materials for covering formation. When it faced separating this from heavy oil etc. and a specific means was adopted after making it immersed for (for example Carboniferous system heavy oils such as tar and a pitch or below petroleum system heavy oil; only saying "heavy oil") it found out that a core surface could manufacture the carbon material uniformly covered in the pitch. And the carbon material particles of the two-layer structure acquired by carrying out in this way are carrying out form which spherical thru/or is approximated to the shape of an ellipsoid or it.

It became clear that form where the edge part of the carbon crystal became round was carried out.

As a result of measurement by a BET adsorption method compared with the core material carbon material before processing, the value of the specific surface area of particles is small and the fine pores which participate in the specific surface area by a BET adsorption method became clear [also being closed with a certain style].

[0010] [whether according to this invention, the carbon material originating in heavy oil etc. adheres to the edge of a carbon material and some or all of a basal lateral used as a core material and] Or some or all of edge and a basal lateral is covered with this carbon material and the particle state coating carbon material almost spherical thru/or being an ellipsoid-like is provided. In this carbon material, the fine pores which participate in the specific surface area measured by a BET adsorption method are closed by the carbonaceous adhesion or covering originating in heavy oil etc. and specific surface area is below $5\text{ m}^2/\text{g}$ (preferably $1\text{--}5\text{ m}^2/\text{g}$ grade).

[0011]In this invention the average spacing (d_{002}) of the field by an X ray wide angle diffraction method (002) as a carbon material used as a core material 0.335-0.340 nm(002) The microcrystal thickness (L_c) of a plane direction uses the high crystalline graphite material whose not less than (preferably not less than 40 nm) 10 nm and microcrystal thickness (L_a) of a plane direction (110) are not less than (preferably not less than 50 nm) 10 nm.

[0012]In the carbon material by this invention it is the feature that the degree of crystallinity of the carbon material (henceforth the carbon material for covering formation) which adhered to the core surface or has covered the core surface is low compared with the degree of crystallinity of the above-mentioned core material.

[0013]The value of the true specific gravity of the carbon material by this invention is in the range of 1.50-2.26 g / cm³.

[0014]When adopting such a carbon material as a negative pole material of a lithium secondary battery it is high capacity and a lithium secondary battery with high safety can be obtained.

[0015]The above coating carbon materials by this invention are manufactured as follows.

First the carbon material used as a core material is preferably immersed in heavy oil of Carboniferous system such as tar and a pitch or a petroleum system etc. at about 10-300

**It dries after adding an organic solvent to the coating carbon material separated after covering with heavy oil etc. and separating this covering core material carbon material from heavy oil etc. subsequently and washing at about 10-300 ** preferably.

[0016]This invention also provides the manufacturing method of the carbon material which carries out carbonization calcination of the coating carbon material covered with the heavy oil etc. which were produced by performing it above and the manufacturing method of the carbon material which carries out graphitization calcination of the coating carbon material covered with the heavy oil produced by performing it above.

[0017]In this invention it is preferred to make it the particle of 1 micrometer or less by laser diffraction type particle-size-distribution measurement become 10% or less of the whole with the integrated value of a volume reference in the carbon material obtained by the above-mentioned manufacturing method.

[0018]In this invention it is preferred to use tar or the pitch which removed at least a part of primary Q and primary QI which remains made 3% or less (preferably 1% or less) as heavy oil which immerses a carbon material.

[0019]The anode for lithium secondary batteries using the negative pole material for lithium secondary batteries wherein this invention makes a component above-mentioned carbonization or the charge of a graphitized carbon material and this negative pole material the nonaqueous lithium secondary battery using this anode and a solid electrolyte secondary cell are provided further.

[0020]When the carbon material which "is [almost spherical or] an ellipsoid-like" in this invention is observed by SEM etc. have inherited the form of the carbon material particles which are core materials but. All or the carbon ingredient which originates in a fuel oil etc. in part of the edge of the carbon material which is a core material and basal laterals adheres and the carbon material in the state where the angle is lost is also included.

Although such a carbon material is efficiently manufactured in the manufacturing method of the invention in this application which does not include a crushing step after covering and calcination In this invention which is not what is limited to the material produced by

this manufacturing method The carbon material in which the fine pores which participate in the specific surface area measured by a BET adsorption method originate in a Carboniferous system or petroleum system heavy oil, such as the raw material for carbon materials for covering formation, i.e., tar, and a pitch, etc. adheres. Or it is covered with such a carbon material and the fine pores which participate in the specific surface area measured by a BET adsorption method include the state where it is selectively closed at least by the fired material (this is called carbon material for covering formation) of the raw material for carbon materials for covering formation, with carbon material with which it is closed. That is fine pores do not need to be thoroughly buried with the carbon material originating in heavy oil etc. for example a carbon material adheres only near the entrance of fine pores and the carbon material which has the fine pores with which the entrance was plugged up is also included. Such a state is checked when specific surface area is measured with a BET adsorption method and specific surface area is small.

[0021] Four combination on the carbon material obtained by this invention and of a low crystal carbon material + low crystal carbon material; low crystal carbon material + quantity crystallinity carbon material; quantity crystallinity carbon material + low crystal carbon material; quantity crystallinity carbon material + quantity crystallinity carbon material is possible The effect of reducing disassembly of an electrolysis solution etc. in all the cases is acquired.

[0022] In this invention low crystal carbon means "the carbon which cannot serve as graphite crystals even if it carries out processing (for example high temperature processing) needed since it graphitizes" and such carbon is usually called hard carbon. High crystallinity carbon means "the carbon which serves as graphite crystals by carrying out processing and processing carried out since it graphitizes" and such carbon is usually called soft carbon.

[0023] the exterior carbon material ("the carbon material for covering formation".) originating in the heavy oil etc. which adhered to the core material and the core material or have covered the core material in this invention The carbon material which has the following eight kinds of composition is obtained by adjustment of the combination which may be called "the carbon material for surface treatment" covering material etc. and the last calcination temperature. Namely carbon material by which ** carbonization processing was carried out and in which a core material consists of a low crystal carbon material and the carbon material for covering formation consists of a low crystal carbon material;

** Carbon material by which carbonization processing was carried out and in which a core material consists of a low crystal carbon material and the carbon material for covering formation consists of a high crystallinity carbon material;

** Carbon material by which conducting graphitization treatment was carried out and in which a core material consists of a low crystal carbon material and the carbon material for covering formation consists of a low crystal carbon material;

** Carbon material by which conducting graphitization treatment was carried out and in which a core material consists of a low crystal carbon material and the carbon material for covering formation consists of a high crystallinity carbon material;

** Carbon material by which carbonization processing was carried out and in which a core material consists of a high crystallinity carbon material and the carbon material for covering formation consists of a low crystal carbon material;

** Carbon material by which carbonization processing was carried out and in which a core material consists of a high crystallinity carbon material and the carbon material for covering formation consists of a high crystallinity carbon material;

** The carbon material by which conducting graphitization treatment was carried out and in which a core material consists of a high crystallinity carbon material and the carbon material for covering formation consists of a low crystal carbon material; and ** conducting graphitization treatment is the carbon material which was carried out and in which a core material consists of a high crystallinity carbon material and the carbon material for covering formation consists of a high crystallinity carbon material.

[0024] An exterior carbon material covers a core material in this invention. Therefore specific surface area is small and the carbon material for rechargeable batteries excellent in charge/discharge capability can be obtained efficiently. According to the combination of the core material and covering material which are especially shown in above **** and ** according to the combination of the core material and covering material which the carbon material for cells which was remarkably excellent in charge/discharge capability is obtained and are shown in ***** and ** specific surface area is small and the carbon material for cells which can improve the safety of a cell is obtained.

[0025] In this invention a carbon material used as a core material One sort of natural graphite of particle state (the shape of a scale thru/or mass fibrous whisker shape a globular shape a granular type etc.) an artificial graphite meso carbon micro beads mesophase pitch powder isotropic pitch powder a resinous coal each carbonization article and a graphitization article or two sorts or more can be used. Also in these the shape of a scale thru/or massive natural graphite and an artificial graphite are dramatically inexpensive they are preferred from the field of cost. Since the carbonization article and graphitization article of meso carbon micro beads (MCMB) are material with dramatically small specific surface area and material with smaller specific surface area can obtain them when using it as a core material they are preferred from the field of the safety of a rechargeable battery.

[0026] As a carbon material used as a core material still more preferably The average spacing (d_{002}) of the field by an X ray wide angle diffraction method (002) is 0.335-0.340 nm and the microcrystal thickness (L_c) of a plane direction (002) is not less than (preferably) 10 nm. Not less than 40 nm and the microcrystal thickness (L_a) of a plane direction (110) are not less than (preferably) 10 nm. It is preferred that the peak intensity ratio near 1360cm^{-1} to the peak intensity ratio not less than 50 nm and near [by argon laser Raman] 1580cm^{-1} (it is henceforth described as an R value) is 0.5 (0.4 or less [Preferably]) or less. When an average spacing is larger than 0.340 nm when L_c and L_a are smaller than 10 nm or when an R value exceeds 0.5 The crystallinity of a carbon material is not enough and since the capacity of the low potential portion (it is 0-300 mV at the potential standard of Li) near a dissolution deposit of lithium becomes less enough when a coating carbon material is produced it is not desirable.

[0027] As for the particle size distribution of the carbon material used as a core material it is preferred that it is about 0.1-150 micrometers. In order to depend for the particle diameter of the ultimate product containing the carbon material for covering formation originating in heavy oil etc. on the particle diameter of the carbon material which is a core material substantially the particle diameter of an ultimate product will also be mostly

prescribed by the particle diameter of a core material. When the particle diameter of a core material is smaller than 0.1 micrometer, the homogeneity of an electrode, the pack density of an active material, the handleability on the process of producing an electrode, fall in becoming larger than 150 micrometers to the danger of causing an internal short circuit through the hole of the separator of a cell becoming high, neither is preferred.

[0028] As for the weight ratio of the carbon material for covering formation originating in heavy oil, i.e. carbon material/for covering formation (carbon material for core material/carbon material + covering formation) (below as for this ratio is called "covering ratio"), it is preferred that it is 0.3 or less, more greatly than 0, and it is more preferred that it is 0.01-0.2. In this case, the thickness of covering carbon serves as the range of about 0.01-10 micrometers, and still more desirable thickness is about 0.05-5 micrometers.

[0029] When the covering ratio exceeded 0.3 and a cell is produced since the capacity in the low voltage portion originating in a core material decreases, it becomes difficult to obtain sufficient capacity. The quantity of covering carbon here is the value which conducted solvent analysis about the carbon ingredient originating in the heavy oil etc. which have covered the circumference of the core material before calcination, and measured the quantity of quinoline soluble. A carbon material is a sphere while the thickness of the carbon material for covering formation measures the diameter of a centriole of the carbon material before covering which serves as a core material with a laser diffraction type particle-size-distribution plan (D50) and the diameter of a centriole of the pitch component coating carbon material before calcination (D50). It is the value which computed it as $\{(\text{particle diameter after covering}) - (\text{particle diameter of the charge of covering Machara})\} / 2$ having assumed after calcination that the form of the enveloping layer of a pitch component is maintained.

[0030] In this invention, the combination whose surface carbon material for covering formation is a low crystal from the carbon material of a core material is preferred. The average spacing (d_{002}) of the field by a wide angle X-ray diffraction method (002) is 0.335-0.340 nm, and the microcrystal thickness (Lc) of a plane direction (002) is not less than (preferably) 10 nm. It is preferred that the R value according to [not less than 40 nm and the microcrystal thickness (La) of a plane direction (110)] to not less than (preferably not less than 50 nm) 10 nm and argon laser Raman spectroscopy is 0.5 (0.5 to about [preferably] 1.5) or more. Although a spacing and an R value are the indices of the degree of crystallinity of common black lead by Raman spectroscopy, the physical properties of the surface of material are reflected on the character of these measuring methods to the character of bulk being reflected in a property value in an X-ray diffraction method, that is, the material which fulfills the above-mentioned property value -- as the character of bulk -- high -- though it is material [****] it means that the surface is a low crystal. Since surface crystallinity is high when the material R value after calcination is smaller than 0.5, the selectivity of a solvent is not lost thoroughly. When the average spacing (d_{002}) which is the character as bulk deviates from the range which is 0.335-0.340 nm, change of the potential accompanying the occlusion and discharge of a lithium ion becomes large, and is not preferred.

[0031] The true density of the coating carbon material of the acquired two-layer structure - 1.50-2.26 g / cm³ grade -- desirable -- 1.8-2.26 g / cm³ grade -- they are 2.0-2.26 g / cm³

grade more preferably. Since active material density in an electrode cannot be raised when true density produces an electrode using a low material even if it is a material excellent in the characteristic per weight it is difficult to obtain the cell of high capacity. [0032] As for the particle diameter of a coating carbon material what has particle size distribution in the range of 0.1-150 micrometers is preferred and it is still more preferred in this particle size distribution that a particle of 1 micrometer or less is 10% or less in a volume reference. Since a battery characteristic falls according to increase of specific surface area when a particle of 1 micrometer or less exceeds 10% by a volume reference in particle diameter it is not desirable.

[0033] The coating carbon material obtained by this invention carries out metallic mold restoration in the state of powder and after it carries out application-of-pressure molding it can also obtain the carbon block or graphite block which has a uniform presentation by calcinating.

[0034] As a raw material for carbon materials for covering formation naphthalene phenanthrene An acenaphthylene anthracene triphenylene pyrene a chrysene Aromatic hydrocarbons such as perylene the tar produced by carrying out the polycondensation of these under heat pressing pitches or the tar which uses the mixture of these aromatic hydrocarbon as the main ingredients a pitch asphalt and oil are raised and the origin does not ask a petroleum system and a Carboniferous system. In this Description these raw materials for carbon materials for covering formation may only be called "heavy oil (a petroleum system or a Carboniferous system) etc." Although it becomes disadvantageous in cost it is also possible to use various kinds of thermosetting resin as a raw material for covering formation.

[0035] When using Carboniferous system heavy oil it is preferred to use tar or the pitch which removed at least a part of primary QI which exists in a raw material and made primary QI which remains 3% or less (preferably 1% or less). Primary QI means here the free carbon originally contained in coal tar. If primary QI exists in a raw material the fall of the characteristic at the time of checking carbonization in the case of calcination and mixing into an ultimate product as an about 1-micrometer spherical carbon grain etc. causing the manufacturing process top problem of an electrode or considering it as an electrode may be caused.

[0036] Usually although it is a solid at ordinary temperatures softening melting of the heavy oil is carried out by heating. This temperature it begins to soften is called softening temperature (SP). In order to specify the quality of heavy oil the toluene insoluble at the time of usually carrying out solvent judgment by toluene is used. Although these are typical methods of specifying heavy oil in specifying the quality of heavy oil in this invention arbitrary methods can be chosen suitably.

[0037] In this invention agitation treatment of a carbon material heavy oil etc. used as the above-mentioned core material is mixed and carried out. The mechanical agitation method which is not limited for example uses a ribbon mixer a screw type kneader an omnipotent mixer etc. especially as agitation means is mentioned.

[0038] Although stirring processing conditions (temperature and time) are suitably chosen according to the ingredient of a raw material (a core material and heavy oil for covering) the viscosity of a mixture etc. they are usually about 10-300 **.

It is more preferred to consider it as the range of about 50-200 ** or to also adjust time collectively so that the viscosity of a mixture may be 5000 or less η_{sp} .

Thus it is possible by adjusting the treatment temperature and time at the time of stirring to control the thickness of the enveloping layer (it is also only called an enveloping layer) of the raw material for covering formation. That is by shortening making temperature high and/or time thickness of an enveloping layer can be made small and thickness of an enveloping layer can be enlarged by making temperature low conversely. Since an enveloping layer does not become uniform unless churning is enough it is not desirable. What is necessary is just to choose mixing time suitably since mass production nature becomes low and is not preferred practical when too long although it generally does not have an adverse effect on the description of a product.

[0039] Although it may be any under atmospheric pressure application of pressure and decompression as an atmosphere at the time of churning since familiarity by a core material and heavy oil improves in agitating under decompression it is desirable.

[0040] In this invention if necessary because of enlarging thickness of an enveloping layer which improves familiarity by the core material and an enveloping layer and which makes thickness of an enveloping layer uniform etc. it is also possible to repeat the above-mentioned mixed stirring process two or more times. A cleaning process may be presented once separating the covered core material in advance of the continuing cleaning process.

[0041] Subsequently a cleaning process is presented with the coating carbon material covered with the heavy oil etc. which were produced by performing it above. As an organic solvent used for

washing toluene quinoline acetone hexane benzene xylene methyl naphthalene alcohol
Carboniferous system oil a petroleum system oil etc. are mentioned. In these toluene quinoline acetone benzene xylene methanol Carboniferous system gas oil and middle oil petroleum system gas oil middle oil etc. are more preferred. Since the insoluble matter in a washing solvent can newly be given to an enveloping layer when choosing these organic solvents suitably it is also possible to control the heavy oil ingredient of an enveloping layer.

[0042] Although what is necessary is just to define washing temperature in consideration of the description etc. of the coating carbon material obtained eventually especially its surface coated layer and it is not limited in particular its about 10-300 °C is preferred.

[0043] As for the rate of the solid in the case of washing {= core material + enveloping layer thru/or impregnation layer (it is only considered as an enveloping layer below)} and an organic solvent it is preferred that it is the range of 1:0.1-10 in a weight ratio.

[0044] In a cleaning process it is possible by choosing the kind of solvent cleaning time washing temperature etc. to adjust the thickness of an enveloping layer the heavy oil ingredient which remains etc. For example in combining suitably conditions such as using a solvent with a weak detergency and making washing temperature low to the thickness of an enveloping layer becoming thin about conditions such as using a solvent with a strong detergency and making washing temperature high in combining **** it becomes possible to thicken thickness of an enveloping layer. What is necessary is just to choose cleaning time suitably in consideration of the above-mentioned monograph affair.

[0045] Subsequently the partition process of a coating carbon material and an organic solvent is performed by techniques such as centrifugal separation and gravity settling. The temperature at the time of dissociating is usually in the range of about 10-300 °C.

[0046]Desiccation of the separated coating carbon material is usually performed in 100-400 °C.

[0047]Thus the obtained dry coating carbon material does not have carbonization treatment and that the pitch component of the circumference of a core material particle is maintained and particles weld thru or condense even if it performs conducting graphitization treatment further.

[0048]Subsequently the coating carbon material dried above is calcinated. When carbonizing a coating carbon material it is possible to calcinate at the temperature of about 600-2000 °C and it is more preferred to calcinate at the temperature which is about 900-1300 °C. When it graphitizes at the temperature of about 2000-3000 °C calcinating is possible. It is more preferred to calcinate at the temperature of about 2500-3000 °C.

[0049]In order to maintain a low crystal calcinating at the elevated temperature on carbonization or graphitization conditions it is also possible for oxidizing gases such as oxygen, carbon monoxide and SO₂ to perform difficulty conducting graphitization treatment in a low-temperature degree region (about 50-400 °C) and to calcinate at an elevated temperature after that to the covered heavy oil layer in advance of calcination of a coating carbon material. For example after making the enveloping layer of high crystallinity form in the core material of high crystallinity it is also possible by performing oxidation treatment to change an enveloping layer into low crystal carbon. On the contrary when not performing such oxidation treatment it is also possible to maintain an enveloping layer in the state of high crystallinity. Such oxidation treatment is performed in advance of carbonization calcination of a coating carbon material. In this case the carbon material obtained is useful as a lithium secondary battery negative electrode material.

[0050]As an atmosphere at the time of calcination of a coating carbon material non-oxidizing atmosphere such as a sealed state of inactive gas and a vacuum are mentioned among reducing atmosphere and an inactive gas atmosphere. Irrespective of calcination temperature a heating rate is suitably chosen from the range about 1-300 °C/hr and firing time is 6 hours - about one month. Temperature up can also be gradually carried out according to the thickness of an enveloping layer etc.

[0051]When performing vacuum carbonization it is preferred to continue a reduced pressure state from ordinary temperature to the highest arrival temperature or to consider it as a reduced pressure state in a suitable temperature region (preferably not less than 500 °C). Vacuum carbonization is effective in removing the surface functional group of a coating carbon material and can reduce the irreversible capacity of a cell.

[0052]Generally at a late heating rate (below 10 °C/hr) formation of a precise enveloping layer is expectable to improvement in mass production nature being expectable at a quick heating rate. It is possible to take various forms such as linear temperature up and gradual temperature up which holds temperature with a constant interval as a temperature profile at the time of temperature up and calcination.

[0053]Since reactivity with the organic solvent of an electrolysis solution is low when the circumference acquired by carrying out such uses the carbon material covered with the carbon material for covering formation as a lithium secondary battery anode neither disassembly of an electrolysis solution nor destruction of a carbon material takes place easily. As a result the charge and discharge efficiency of a cell improves and it has the advantage that the safety is improved. Generally since the end face (edge plane) of

activity microcrystal is carrying out orientation of the material of a black lead system outside it reacts to an electrolysis solution easily. In this invention the pitch component in which the basolateral (basal plane) which is carbonaceous condensed multi-ring meshes of a net is carrying out orientation outside has covered this activity microcrystal end face. Therefore it is thought that a reaction with the organic solvent of an electrolysis solution is controlled.

[0054] The quantity of covering heavy oil of the circumference of a carbon material thru or the thickness of an enveloping layer are controllable by this invention by adjusting a kind of cleaning condition (time, temperature, etc.) of an organic solvent at the time of washing the temperature which immerses the carbon material which is a core material in heavy oil, etc. time of the covered carbon material. Therefore the basolateral which is carbonaceous condensed multi-ring meshes of a net can manufacture the carbon material which had the surface covered by the pitch component which is carrying out orientation in the direction of the surface of a carbon material.

[0055] Carbonization or the state where the basolateral carried out orientation in the direction of the surface of a carbon material in covering of a core surface even if graphitized further is maintained in these carbon materials. Therefore since it is hard to react to the organic solvent of an electrolysis solution in using this carbon material for a lithium secondary battery anode, neither disassembly of an electrolysis solution nor destruction of a carbon material takes place. As a result, the charge and discharge efficiency of a cell serves as a high value and the prominent effect of excelling also in the safety of a cell is acquired.

[0056] After presenting processing of distribution, cracking, a classification, etc. with the coating carbon material produced by making it above if necessary in producing the lithium secondary battery by the invention in this application, it adjusts to a suitable particle size and is considered as an electrode material.

[0057] An electrode is publicly known -- a binder -- after mixing. An active material layer is formed on a charge collector. Especially as a binder, it is not limited but polyolefin system polymer; synthetic rubbers such as fluorine system polymer; polyethylenes such as polytetrafluoroethylene and polyvinylidene fluoride and polypropylene can be used. As a quantity of the binder in this case, it is usually the range of about 3-50 weight sections to active material, 100 weight section and is about 5-20 weight sections more preferably and they are about 5-15 weight sections still more preferably. Since the density of the active material in an electrode will fall if there is too much quantity of a binder, it is not desirable. Since the capability to hold the active material in an electrode will not be obtained enough but the stability of an electrode will fall if there are too few binders, it is not desirable. The paste which mixed the active material and the binder is produced as a method of forming an electrode. The method of forming an active material layer on a charge collector by doctor blade, a bar coating machine, etc. or the method of putting into a molding machine, etc. what mixed the active material and the binder and using as a plastic solid with a press, etc. is mentioned.

[0058] As an electrolyte of the lithium secondary battery by the invention in this application, publicly known organic electrolysis liquid, an inorganic solid electrolyte, a solid polymer electrolyte, etc. can be used.

[0059] Also in these the viewpoint of ionic conductivity to especially organic electrolysis liquid is preferred. As a solvent for organic electrolysis liquid propylene carbonate, ethylene carbonate, butylene carbonate, diethyl carbonate, dimethyl carbonate, ester species such as methyl ethyl carbonate and gamma-butyrolactone; A tetrahydrofuran. Substitution tetrahydrofuran such as 2-methyltetrahydrofuran; Dioxolane. Ethers such as diethylether, dimethoxyethane, diethoxyethane and methoxyethoxy ethane; Dimethyl sulfoxide. Sulfonamethyl sulfonate, acetonitrile, methyl formate, methyl acetate, etc. are illustrated. It is independent of these can be mixed and used. As an electrolyte, lithium perchlorate, lithium borofluoride, 6 fluorination [phosphoric acid] lithium. Lithium salts such as 6 fluorination lithium arsenate and lithium trifluoromethanesulfonate, lithium halide, ulmin acid, lithium chloride, etc. are illustrated and these one sort or two sorts or more can be used. Organic electrolysis liquid is prepared by dissolving an electrolyte in the above-mentioned solvent. It cannot be overemphasized that the solvent and electrolyte which are used when preparing an electrolysis solution are not limited to what was hung up above.

[0060] As an inorganic solid electrolyte, they are mentioned by the nitride of Li, a halogenide, an oxygen acid salt, the phosphorus sulfide compound, etc. and more specifically Li_3N , LiLiLi_3N , Li-Li-OH , LiSiO_4 and $\text{LiSiO}_4\text{-Li-Li-OH}$, $\text{Li}_3\text{PO}_4\text{-Li}_4\text{SiO}_4\text{Li}_2\text{Si}_3\text{S}_3$, etc. are illustrated.

[0061] There are a substance which comprised a polymer which performs dissociation of the above-mentioned electrolyte and an electrolyte, a substance which gave the ionic dissociation group to the polymer, etc. in an organic solid electrolyte. There are polymer, phosphoric ester polymer, etc. which contain polymer, the polypropylene oxide derivative, and this derivative containing a polyethylene oxide derivative and this derivative as a polymer which dissociates an electrolyte, for example. The material which added polyacrylonitrile to the mixture of the polymer matrix material which made the above-mentioned aprotic polar solvent contain polymer containing an ionic dissociation group and the above-mentioned aprotic polar solvent and the electrolysis solution is also usable. It is also possible to use together an inorganic solid electrolyte and an organic solid electrolyte.

[0062] As a cathode in the lithium secondary battery of this invention, the oxide which contains lithium, for example, can be used as positive active material in accordance with a conventional method. As a concrete example of positive active material, LiCoO_2 , LiNiO_2 , LiFeO_2 , LiMnO_2 , $\text{Li}_x\text{M}_y\text{N}_z\text{O}_2$ that is these relative compounds (M here) [Fe and]. Are either Co, nickel and Mn and N expresses a transition metal, 4B group metal, 5B group metal. LiMn_2O_4 and $\text{LiMn}_{2-x}\text{N}_x\text{O}_4$ (here -- N -- a transition metal.) which is the relative compound LiVO_2 showing 4B group metal or 5B group metal, etc. are mentioned depending on a conducting material, a binder, and the case, a solid electrolyte, etc. are mixed to this and a cathode is formed in it. The mixture ratio of these each material can be used as about 5-50 weight sections of conducting materials and about 1-30 weight sections of binders to active material, 100 weight section. Especially as such a conducting material, it is not restricted but carbons such as publicly known carbon black (acetylene black, thermal black, channel black, etc.), graphite powder, metal powder, etc. can be used and it is **. It is not limited in particular as a binder but polyolefin system polymer; synthetic rubbers such as fluorine system polymer; polyethylenes such as publicly known polytetrafluoroethylene and polyvinylidene fluoride and polypropylene can be used. The

loadings of a conducting material are smaller than five weight sections or since resistance or polarization of an electrode etc. becomes large and service capacity becomes small when the loadings of a binder are larger than 30 weight sections a practical lithium secondary battery is unproducible. Since the amount of active materials contained in an electrode becomes less when there are more conducting materials than 50 weight sections (the relative rate changes according to the kind of conducting material to mix) the service capacity as a cathode becomes small. To binding capability being lost if a binder is smaller than one weight section if larger than 30 weight sections Since the amount of active materials contained in an electrode becomes less like the case of a conducting material resistance or polarization of an electrode etc. becomes large like a description further at the above and service capacity becomes small it is not practical. In order to raise a binding property when producing a cathode it is preferred to heat-treat at the temperature near the melting point of each binder.

[0063] As a separator for holding an electrolysis solution the Plastic solid of powders such as nonwoven fabrics such as plastic fiber of publicly known electric insulation glass fiber and a natural fiber or textile fabrics and alumina etc. are mentioned. Also in these nonwoven fabrics which are synthetic resins such as polyethylene and polypropylene are preferred from points such as the stability of quality. When a cell carries out an abnormal heat generation a separator dissolves in the nonwoven fabric of these synthetic resins with heat there are some which added the function which intercepts between a cathode and anodes in it and these can also be conveniently used for it from a viewpoint of safety. The thickness in particular of a separator is not limited but can hold the electrolysis solution of an initial complement and just prevents the short circuit of a cathode and an anode is usually about 0.01-1 mm and is about 0.02-0.05 mm preferably. [0064] Although the foil form of metals such as publicly known copper nickel stainless steel aluminum and titanium mesh a porous body etc. are illustrated as a charge collector it is not limited to these.

[0065] ** ** In effect this invention a carbon material especially the material of a high black lead system of crystallinity Tar After being immersed in a Carboniferous system or petroleum system heavy oils such as a pitch etc. and separating the covered carbon material from heavy oil etc. the surface of the carbon material as a core material can obtain the new carbon material covered with heavy oil etc. by washing and drying with an organic solvent.

[0066] When the surface carbonizes the carbon material of a black lead system uniformly covered in the pitch at 600 °C - 2000 °C a core material consists of material of a black lead system with a high degree of crystallinity and the surface can manufacture the carbon material of a unique structure where it is covered with the material of a carbon system with a low degree of crystallinity.

[0067] Since according to the manufacturing method of the invention in this application weld thru or condensation of particles is not produced even when washing desiccation and calcination are performed after covering the carbon material which is a core material with heavy oils such as a pitch and Tar It is not necessary to grind the obtained carbon material and particles near what is called in the shape of ["that was able to take the angle"] a ball are obtained. The degradation factor of a material called mixing of the impurity accompanying grinding does not exist either.

[0068] In producing a nonaqueous secondary battery or a solid electrolyte cell using the

coating carbon material obtained by this invention especially the carbon material which covered the surface of the graphite material with those fired materials such as heavy oil becomes possible to manufacture the cell excellent in both a charging and discharging characteristic and safety.

[0069] Inexpensive natural graphite, artificial graphite, etc. are used as a core material, a pitch, inexpensive also as covering material, etc. are used. The manufacturing method is also simple for this invention method and since it is a manufacturing method which was dramatically excellent also in mass production nature, it can obtain the inexpensive negative pole material for highly efficient lithium secondary batteries.

[0070] In this invention, the combination of a core material and facing A low crystal carbon material + low crystal carbon material, a low crystal carbon material + quantity crystallinity carbon material, Four kinds of combination of a high crystallinity carbon material + low crystal carbon material and a high crystallinity carbon material + quantity crystallinity carbon material are possible and if two more baking processes (carbonization, calcination and graphitization, calcination) are taken into consideration, eight sorts of carbon materials will be obtained. Among these, the high crystallinity carbon material + low crystal carbon material and high crystallinity carbon material + quantity crystallinity carbon material by which carbonization processing was carried out. When using the carbon material which consists of combination of the high crystallinity carbon material + low crystal carbon material, etc. by which conducting graphitization treatment was carried out, reactivity with an electrolysis solution is low and since the outstanding charging and discharging characteristic is demonstrated, it is especially useful as a negative pole material for lithium secondary batteries.

[0071] A below form embodiment best [for inventing] explains invention concretely. Various kinds of measurement in each following embodiment was performed as follows.

1. The diameter of a centriole and particle size distribution of particles were measured using the "9220 micro of FRA(s) track" by measurement NIKKISO CO. LTD. of particle diameter.

2. About the carbon ingredient of the heavy oil origin which has covered a covering ratio and the circumference of a core material before measurement, calcination of covering thickness. Solvent analysis was conducted according to the method specified to JIS K2425 quinoline insoluble (%) was measured and quinoline soluble (%) was computed by "100 - (quinoline insoluble)." The quantity of this quinoline soluble is the quantity of the carbon material for covering formation.

[0072] The weight ratio (covering ratio defined previously) of carbon material/for covering formation (carbon material for core material, carbon material + covering formation) was computed by the above-mentioned method.

3. Specific surface area was measured using the "ASAP2400/nitrogen absorption BET specific surface area measuring device" by measurement Micromeritics of specific surface area.

4. True specific gravity was measured according to the method specified to measurement JIS R7212 of true specific gravity.

5. Method 55-631.e. carbon material experimental technique 1 pp, that measurement of size (Lc, La) of microcrystal by measurement X-rays wide angle diffraction method of size of microcrystal by X ray wide angle diffraction method is publicly known. It carried out by the method indicated to edited (technology company) by the Carbon Society of

Japan. The form factor K which asks for the size of microcrystal used 0.9.

6. The R value was calculated as a peak intensity ratio of $1360\text{cm}^{-1}/1580\text{cm}^{-1}$ from two peaks observed by the Raman spectrometry which used a 514.5-nm argon laser for the Raman spectrometry pan as a surface physical property of a carbon material.

7. It graphitized by dipping an anode in an electrolysis solution and calculating the measuring pitch coating carbon material (pitch covering black lead) of the gas yield at the time of holding at an elevated temperature at 2800 °C among a nitrogen atmosphere for 1 hour. After mixing graphitization pitch covering black lead 95 weight section and PTFE("D-1" by DAIKIN INDUSTRIES LTD.) 5 dispersion type weight section and stirring uniformly by the liquid phase it was made to dry and was considered as paste state. After molding this substance 0.25g for anodes with the pressing machine and producing a negative electrode body 2 cm in diameter vacuum drying was carried out at 200 °C for 6 hours.

[0073] Subsequently this anode was charged until potential was set to 0V in the electrolysis solution the anode of the charging state was put into the beaker cell of 25 ml of electrolysis solutions which entered it heated at 60 °C for 6 hours and the gas yield of per graphitization pitch covering black lead 1g was measured.

[0074] As an electrolysis solution the mixed solvent (it is 3:3:4 at a volume ratio) of ethylene carbonate, diethyl carbonate and methyl propionate in which LiClO_4 of 1mol dm^{-3} was dissolved was used.

8. Production of a nonaqueous cell and the measurement cathode of a battery characteristic are generally produced by mixing a positive electrode material a conducting material and a binder. In this case as a conducting material metallic materials such as carbon material such as carbon black and black lead or metal powder and metal wool yarn etc. are used suitably. Although it is also mixable with powder a binder may mix the thing which the solution was made to distribute and the dissolved thing in order to improve dispersibility more and to improve a binding property. When what was carried out in this way and was distributed or dissolved in the solution is used it is necessary to remove a solution by vacuum treating heat treatment or other means. It is also possible by furthermore heat-treating at the temperature near the melting point depending on the kind of binder to improve a binding property further.

[0075] LiCoO_2 100 weight section was used for the positive electrode material what mixed ten weight sections of PTFE powder by using acetylene black as a conducting material as ten weight sections and a binder was fabricated in working example in this application to an electrode 10 mm in diameter and the positive electrode body was obtained.

[0076] The negative electrode body was produced as follows by working example in this application.

[0077] First pitch covering black lead was calcinated at 1000 °C among a nitrogen atmosphere for 1 hour and it carbonized. After mixing this carbonization pitch covering black lead 95 weight section and PTFE("D-1" by DAIKIN INDUSTRIES LTD.) 5 dispersion type weight section and stirring uniformly by the liquid phase it was made to dry and was considered as paste state. After molding 30 mg of this substance for anodes with the pressing machine and producing a negative electrode body 10 mm in diameter vacuum drying was carried out at 200 °C for 6 hours.

[0078] Among a nitrogen atmosphere at 2800 °C pitch covering black lead was calcinated for 1 hour and was graphitized. After mixing this graphitization pitch covering black lead

95 weight section and PTFE("D-1" by DAIKIN INDUSTRIES LTD.) 5 dispersion type weight section and stirring uniformly by the liquid phase it was made to dry and was considered as paste state. After molding 30 mg of this substance for anodes with the pressing machine and producing a negative electrode body 10 mm in diameter vacuum drying was carried out at 200 °C for 6 hours.

[0079] The polypropylene non-woven fabric was used as a separator.

[0080] When carbonization pitch covering black lead was used as a negative electrode body the propylene carbonate in which LiClO_4 of 1 moldm⁻³ was dissolved was used for the electrolysis solution. When graphitization pitch covering black lead was used the mixed solvent (it is 3:3:4 at a volume ratio) of ethylene carbonate diethyl carbonate and methylpropionate in which LiClO_4 of 1 moldm⁻³ was dissolved was used.

[0081] The discharge characteristic of the coin type lithium secondary battery produced using the positive electrode body the negative electrode body separator and electrolysis solution which were produced by performing it above was measured. Measurement was carried out under the constant current charge and discharge of 1 mA / cm² and service capacity was made into capacity until cell voltage falls to 1.2V.

9. Both sides of 0.02-mm-thick copper foil were plastered with the paste state anode substance produced like the clauses (above-mentioned 8.) of production of a solid electrolyte cell and production of the measurement nonaqueous cell of a battery characteristic and it dried and it rolled and was considered as a negative electrode plate 0.10 mm in thickness 55 mm in width and 90 mm in length.

[0082] Polyethylene oxide (molecular weight 600000) and LiClO_4 are dissolved in acetonitrile. After casting this solution on a PTFE film (the "Teflon" by Du Pont) in the glove box of argon atmosphere it was neglected at 25 °C among the glove box the solvent was evaporated it dried further and $\text{P}(\text{FEO})_8$ and LiClO_4 of the solid electrolyte were prepared.

[0083] The film mold lithium secondary battery was produced using $\text{P}(\text{FEO})_8$ and LiClO_4 as a solid electrolyte using LiCoO_2 as carbonization pitch covering black lead or graphitization pitch covering black lead solid electrolyte and positive electrode body as a negative electrode body obtained above.

[0084] The discharge characteristic of the lithium secondary battery obtained above was measured. Measurement was carried out under the constant current charge and discharge of 1 mA / cm² and service capacity was made into capacity until cell voltage falls to 1.2V. An embodiment 1 massive artificial graphite (diameter D of centre hole 50 = 7.5 micrometer and 0.1-150 micrometers of particle size distribution) d002 = 0.336 nm / La = 97 nm specific surface area = 10.8 m² / g R value = 0.26 true-specific-gravity = 2.25 g / cm³ 50 g and the coal tar pitch of 80 °C of softening temperatures that removed primary QI beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 500-ml SEPARER flask agitation mixing was carried out by 200 °C and ordinary pressure for 2 hours and crude pitch covering black lead was obtained. After adding one copy of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 80 °C under churning for 1 hour it filtered and refined pitch covering black lead was obtained. It was 7.7 micrometers when the diameter D50 of a centre hole of this refined pitch covering black lead was measured. Since the diameter D50 of a centre hole of black lead as a core material was 7.5 micrometer the thickness of a pitch layer is 0.1 micrometer.

[0085] The quinoline soluble specific surface area and true specific gravity of the obtained

refined pitch covering black lead are shown in Table 1. Since the value of quinoline soluble is 9.6% the covering ratio of this refined pitch covering black lead is 0.096. [0086] This refined pitch covering black lead was calcinated at 1000 °C among a nitrogen atmosphere for 1 hour (the heating rate of 25 °C / hr) and it carbonized. The specific surface area of the obtained carbonization pitch covering black lead true specific gravimetric R value and the volume reference integrated value of a particle of 1 micrometer or less are shown in Table 1. As a result of particle-size-distribution measurement of this refined pitch covering black lead having distribution in 0.1-150 micrometers like a core material was checked and the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and carbonization pitch covering black lead. As a result of SEM observation the artificial graphite which is a core material was covered with the carbonization pitch which forms an enveloping layer and it was checked that the edge part is round.

[0087] This carbonization pitch covering black lead was used the anode was produced and the nonaqueous secondary battery was produced using the propylene carbonate in which LiClO_4 of 1 mol/dm³ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is shown in Table 2.

[0088] Carbonization pitch covering black lead was used the anode was produced and the solid electrolyte lithium secondary battery was produced. The charge-and-discharge characteristic measurement result is shown in Table 3.

The refined pitch covering black lead produced by making it be the same as that of embodiment 2 Embodiment 1 was calcinated at 1000 °C under the vacuum of 10 torr for 1 hour (the heating rate of 25 °C / hr) and vacuum carbonization was carried out. The specific surface area of the obtained vacuum carbonization pitch covering black lead true specific gravimetric R value and the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1 and are shown. As a result of particle-size-distribution measurement of this vacuum carbonization pitch covering black lead having distribution in 0.1-150 micrometers like a core material was checked and the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and vacuum carbonization pitch covering black lead. As a result of SEM observation the artificial graphite which is a core material was covered with the vacuum carbonization pitch which forms an enveloping layer and it was checked that the edge part is round.

[0089] The anode was produced using this vacuum carbonization pitch covering black lead and the nonaqueous secondary battery was produced using the propylene carbonate in which LiClO_4 of 1 mol/dm³ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2 and is shown. Among a nitrogen atmosphere at 2800 °C the refined pitch covering black lead produced by making it be the same as that of embodiment 3 Embodiment 1 was calcinated for 1 hour and was graphitized. The specific surface area of the obtained graphitization pitch covering black lead true specific gravimetric R value and the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1 and are shown. As a result of particle-size-distribution measurement of this graphitization pitch covering black

leadhaving distribution in 0.1-150 micrometers like a core material was checkedand the X diffraction measurement result was the same as that of a core material. The graphitization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and graphitization pitch covering black lead. As a result of SEM observationthe artificial graphite which is a core material was covered with the graphitization pitch which forms an enveloping layerand it was checked that the edge part is round.

[0090]The anode was produced using this graphitization pitch covering black leadand the nonaqueous secondary battery was produced using the mixed solvent (3:3:4) of ethylene carbonatediethyl carbonateand methylpropionate in which LiClO_4 of 1moldm⁻³ was dissolved as an electrolysis solution.

[0091]The gas yield in the inside of the electrolysis solution of this graphitization pitch covering black lead was measured. The charge-and-discharge characteristic measurement result and gas yield are combined with Table 2and are shown.

In the lead hammer furnace which can do very slow temperature upthe refined pitch covering black lead produced by making it be the same as that of embodiment 4 Embodiment 1 was calcinated at 1000 ** (below reducing atmospherethe heating rate of 5 ** / hr)and it carbonized. The specific surface area of this carbonization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1and are shown. As a result of particle-size-distribution measurement of this carbonization pitch covering black leadhaving distribution in 0.1-150 micrometers like a core material was checkedand the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and carbonization pitch covering black lead. As a result of SEM observationthe artificial graphite which is a core material was covered with the carbonization pitch which forms an enveloping layerand it was checked that the edge part is round.

[0092]The anode was produced using this carbonization pitch covering black leadand the nonaqueous secondary battery was produced using the propylene carbonate in which LiClO_4 of 1moldm⁻³ was dissolved as an electrolysis solution. A charge-and-discharge characteristic measurement result is combined with Table 2and is shown.

The refined pitch covering black lead produced by making it be the same as that of embodiment 5 Embodiment 1 was calcinated at 1300 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr)and it carbonized. The specific surface area of this carbonization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1and are shown. As a result of particle-size-distribution measurement of this carbonization pitch covering black leadhaving distribution in 0.1-150 micrometers like a core material was checkedand the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and carbonization pitch covering black lead. As a result of SEM observationthe artificial graphite which is a core material was covered with the carbonization pitch which forms an enveloping layerand it was checked that the edge part is round.

[0093]The anode was produced using this carbonization pitch covering black lead and the nonaqueous secondary battery was produced using the propylene carbonate in which LiClO_4 of 1 moldm⁻³ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2 and is shown.

The refined pitch covering black lead produced by making it be the same as that of embodiment 6. Embodiment 1 was oxidized at 300 °C among an air atmosphere in the constant temperature/humidity chamber for 8 hours. The covering ratio, specific surface area and true specific gravity of the obtained oxidation refined pitch covering black lead are shown in Table 1. This oxidation refined pitch covering black lead was calcinated at 1000 °C among a nitrogen atmosphere for 1 hour (the heating rate of 25 °C / hr) and it carbonized. The specific surface area of the obtained carbonization pitch covering black lead, true specific gravity, an R value and the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1 and are shown. As a result of particle-size-distribution measurement of this carbonization pitch covering black lead having distribution in 0.1-150 micrometers like a core material was checked and the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and carbonization pitch covering black lead. As a result of SEM observation the artificial graphite which is a core material was covered with the carbonization pitch which forms an enveloping layer and it was checked that the edge part is round.

[0094]The anode was produced using this carbonization pitch covering black lead and the nonaqueous secondary battery was produced using the propylene carbonate in which LiClO_4 of 1 moldm⁻³ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2 and is shown.

An embodiment 7 massive artificial graphite (diameter Dof centriole 50 = 7.5 micrometer, particle size distribution = 0.1-150 micrometers) d002 = 0.336 nm, Lc = 100 nm, La = 97 nm, specific surface area = 10.8 m²/g, R value = 0.26, true-specific-gravity = 2.25 g / cm³, 50g and the coal tar pitch of 80 °C of softening temperatures that removed primary QI beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 500-ml SEPARER U flask, agitation mixing was carried out at 200 °C for 2 hours and crude pitch covering black lead was obtained.

[0095]After adding one copy of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 20 °C under churning for 1 hour it filtered and refined pitch covering black lead was obtained. It was 7.9 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of the artificial graphite as a core material was 7.5 micrometer, the thickness of a pitch layer is 0.2 micrometer.

[0096]The covering ratio, specific surface area and true specific gravity of the obtained refined pitch covering black lead are shown in Table 1. Since the value of quinoline soluble is 20.4%, the covering ratio of this refined pitch covering black lead is 0.204.

[0097]The obtained refined pitch covering black lead was calcinated at 1000 °C among a nitrogen atmosphere for 1 hour (the heating rate of 25 °C / hr) and it carbonized. The specific surface area of this carbonization pitch covering black lead, true specific gravity, an R value and the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1 and are shown. As a result of particle-size-distribution

measurement of this carbonization pitch covering black lead having distribution in 0.1-150 micrometers like a core material was checked and the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and carbonization pitch covering black lead. As a result of SEM observation the artificial graphite which is a core material was covered with the carbonization pitch which forms an enveloping layer and it was checked that the edge part is round.

[0098] The anode was produced using this carbonization pitch covering black lead and the nonaqueous secondary battery was produced using the propylene carbonate in which LiClO_4 of 1mol dm^{-3} was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2 and is shown. Among a nitrogen atmosphere at 2800°C the refined pitch covering black lead produced by making it be the same as that of embodiment 8. Embodiment 7 was calcinated for 1 hour and was graphitized. The specific surface area of the obtained graphitization pitch covering black lead, true specific gravity, R value, and the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1 and are shown. As a result of particle-size-distribution measurement of this graphitization pitch covering black lead having distribution in 0.1-150 micrometers like a core material was checked and the X diffraction measurement result was the same as that of a core material. The graphitization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and graphitization pitch covering black lead. As a result of SEM observation the artificial graphite which is a core material was covered with the graphitization pitch which forms an enveloping layer and it was checked that the edge part is round.

[0099] The anode was produced using this graphitization pitch covering black lead and the nonaqueous secondary battery was produced using the mixed solvent (3:3:4) of ethylene carbonate, diethyl carbonate, and methyl propionate in which LiClO_4 of 1mol dm^{-3} was dissolved as an electrolysis solution. The gas yield in the inside of the electrolysis solution of this graphitization pitch covering black lead was measured. The charge-and-discharge characteristic measurement result and gas yield are combined with Table 2 and are shown.

An embodiment 9 massive artificial graphite (diameter D_{50} of centriole $D_{50} = 7.5\text{ micrometers}$, particle size distribution = 0.1-150 micrometers) $d_{002} = 0.336\text{ nm}$, $L_c = 100\text{ nm}$, $L_a = 97\text{ nm}$, specific surface area = $10.8\text{ m}^2/\text{g}$, R value = 0.26, true-specific-gravity = 2.25 g/cm^3 , 50g and the coal tar pitch of 80% of softening temperatures that removed primary QI beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 500-ml SEPARERU flask, agitation mixing was carried out at 200°C for 2 hours under decompression (they are suction and decompression degree 50 torr with a vacuum pump) and crude pitch covering black lead was obtained.

[0100] After adding one copy of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 80°C under churning for 1 hour, it filtered and refined pitch covering black lead was obtained. It was 7.7 micrometers when the diameter D_{50} of a centriole of this refined pitch covering black lead was measured. Since the diameter D_{50} of a centriole of the artificial graphite which is a core material

was 7.5 micrometer the thickness of a pitch layer is 0.1 micrometer.

[0101] The covering ratio specific surface area and true specific gravity of this refined pitch covering black lead are shown in Table 1. Since the value of quinoline soluble is 10.4% the covering ratio of this refined pitch covering black lead is 0.104.

[0102] This refined pitch covering black lead was calcinated at 1000 °C among a nitrogen atmosphere for 1 hour (the heating rate of 25 °C / hr) and it carbonized. The specific surface area of the obtained carbonization pitch covering black lead true specific gravity γ_R value and the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1 and are shown. As a result of particle-size-distribution measurement of this graphitization pitch covering black lead having distribution in 0.1-150 micrometers like a core material was checked and the X diffraction measurement result was the same as that of a core material. The graphitization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the γ_R value of a core material and graphitization pitch covering black lead. As a result of SEM observation the artificial graphite which is a core material was covered with the graphitization pitch which forms an enveloping layer and it was checked that the edge part is round.

[0103] The anode was produced using this carbonization pitch covering black lead and the nonaqueous secondary battery was produced using the propylene carbonate in which LiClO_4 of 1 mol/dm³ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2 and is shown.

An embodiment 10 massive artificial graphite (diameter Dof centriele 50 = 7.5 micrometer particle size distribution = 0.1-150 micrometers) d002 = 0.336 nm ρ_c = 100 nm ρ_a = 97 nm specific surface area = 10.8 m²/g γ_R value = 0.26 true-specific-gravity = 2.25 g / and cm³ 50 g and the coal tar pitch of 80 °C of softening temperatures that removed primary QI beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 500-ml SEPARER flask agitation mixing was carried out at 200 °C for 2 hours and crude pitch covering black lead was obtained.

[0104] After adding one copy of tar middle oil to one copy of obtained crude pitch covering black lead and carrying out washing processing at 20 °C under churning for 1 hour it filtered and refined pitch covering black lead was obtained. It was 7.6 micrometers when the diameter D50 of a centriele of this refined pitch covering black lead was measured. Since the diameter D50 of a centriele of black lead of a core material was 7.5 micrometer the thickness of a pitch layer is 0.05 micrometer.

[0105] The covering ratio specific surface area and true specific gravity of this refined pitch covering black lead are shown in Table 1. Since the value of quinoline soluble is 8.8% the covering ratio of this refined pitch covering black lead is 0.088.

[0106] This refined pitch covering black lead was calcinated at 1000 °C among a nitrogen atmosphere for 1 hour (the heating rate of 25 °C / hr) and it carbonized. The specific surface area of this carbonization pitch covering black lead true specific gravity γ_R value and the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1 and are shown. As a result of particle-size-distribution measurement of this graphitization pitch covering black lead having distribution in 0.1-150 micrometers like a core material was checked and the X diffraction measurement result was the same as that of a core material. The graphitization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core

material by comparison of the R value of a core material and graphitization pitch covering black lead. As a result of SEM observation the artificial graphite which is a core material was covered with the graphitization pitch which forms an enveloping layer and it was checked that the edge part is round.

[0107] The anode was produced using this carbonization pitch covering black lead and the nonaqueous secondary battery was produced using the propylene carbonate in which LiClO_4 of 1 mol dm^{-3} was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2 and is shown.

An embodiment 11 massive artificial graphite (diameter ϕ of centric circle $50 = 7.5 \text{ micrometer}$, particle size distribution = $0.1\text{--}150 \text{ micrometers}$) $d_{002} = 0.336 \text{ nm}$, $L_c = 100 \text{ nm}$, $L_a = 97 \text{ nm}$, specific surface area = $10.8 \text{ m}^2/\text{g}$, R value = 0.26 , true-specific-gravity = 2.25 g/cm^3 , 50 and the coal tar pitch of $80 \text{ }^\circ\text{C}$ of softening temperatures that removed primary QI beforehand (it and) [quinoline-insoluble-] 200 g of 30% toluene insoluble was put into a 1000-ml SEPARER flask, agitation mixing was carried out at $200 \text{ }^\circ\text{C}$ for 2 hours and crude pitch covering black lead was obtained.

[0108] After adding one copy of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at $80 \text{ }^\circ\text{C}$ under churning for 1 hour, it filtered and refined pitch covering black lead was obtained. It was 7.9 micrometers when the diameter D_{50} of a centric circle of this refined pitch covering black lead was measured. Since the diameter D_{50} of a centric circle of black lead of a core material was 7.5 micrometers , the thickness of a pitch layer is 0.2 micrometer .

[0109] The covering ratio, specific surface area and true specific gravity of this refined pitch covering black lead are shown in Table 1. Since the value of quinoline soluble is 17.3% , the covering ratio is 0.173 .

[0110] This refined pitch covering black lead was calcinated at $1000 \text{ }^\circ\text{C}$ among a nitrogen atmosphere for 1 hour (the heating rate of $25 \text{ }^\circ\text{C/hr}$) and it carbonized. The specific surface area of this carbonization pitch covering black lead, true specific gravity, an R value and the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1 and are shown. As a result of particle-size-distribution measurement of this carbonization pitch covering black lead, having distribution in $0.1\text{--}150 \text{ micrometers}$ like a core material was checked and the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and carbonization pitch covering black lead. As a result of SEM observation the artificial graphite which is a core material was covered with the carbonization pitch which forms an enveloping layer and it was checked that the edge part is round.

[0111] The anode was produced using this carbonization pitch covering black lead and the nonaqueous secondary battery was produced using the propylene carbonate in which LiClO_4 of 1 mol dm^{-3} was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2 and is shown.

An embodiment 12 massive artificial graphite (diameter ϕ of centric circle $50 = 7.5 \text{ micrometer}$, particle size distribution = $0.1\text{--}150 \text{ micrometers}$) $d_{002} = 0.336 \text{ nm}$, $L_c = 100 \text{ nm}$, $L_a = 97 \text{ nm}$, specific surface area = $10.8 \text{ m}^2/\text{g}$, The coal tar pitch of $80 \text{ }^\circ\text{C}$ of softening temperatures which has not removed R value = 0.26 , true-specific-gravity = 2.25 g/cm^3 , 50 and primary QI (3.9% of quinoline insoluble) 100 g of 34%

toluene insoluble was put into a 500-ml SEPARERU flask agitation mixing was carried out at 200 ** under ordinary pressure for 2 hours and crude pitch covering black lead was obtained.

[0112] After adding one copy of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 80 ** under churning for 1 hour it filtered and refined pitch covering black lead was obtained. It was 7.9 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of black lead of a core material was 7.5 micrometers the thickness of a pitch layer is 0.2 micrometer.

[0113] The covering ratio of this refined pitch covering black lead specific surface area and true specific gravity are shown in Table 1. Since the value of quinoline soluble is 7.5% covering ratio is 0.075.

[0114] This refined pitch covering black lead was calcinated at 1000 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr) and it carbonized. The specific surface area of this carbonization pitch covering black lead true specific gravity an R value and the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1 and are shown. As a result of particle-size-distribution measurement of this carbonization pitch covering black lead having distribution in 0.1-150 micrometers like a core material was checked and the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and carbonization pitch covering black lead. As a result of SEM observation the artificial graphite which is a core material was covered with the carbonization pitch which forms an enveloping layer and it was checked that the edge part is round.

[0115] The anode was produced using this carbonization pitch covering black lead and the nonaqueous secondary battery was produced using the propylene carbonate in which LiClO_4 of 1mol dm^{-3} was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2 and is shown.

An embodiment 13 massive artificial graphite (diameter D of centriole $50=7.5\text{micrometer}$ particle size distribution = 0.1-150 micrometers) $d_{002}=0.336\text{nm}$ $L_c=100\text{nm}$ $L_a=97\text{nm}$ specific surface area $=10.8\text{m}^2/\text{g}$ R value $=0.26$ true-specific-gravity $=2.25\text{g}/\text{cm}^3$ 50g and coal tar of 10 ** of softening temperatures from which primary QI was removed beforehand (it and) [quinoline-insoluble-] 100 g of 8% toluene insoluble was put into a 500-ml SEPARERU flask agitation mixing was carried out at 200 ** under ordinary pressure for 2 hours and crude pitch covering black lead was obtained.

[0116] After adding one copy of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 80 ** under churning for 1 hour it filtered and refined pitch covering black lead was obtained. It was 7.6 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of black lead of a core material was 7.5 micrometers the thickness of a pitch layer is 0.05 micrometer.

[0117] The covering ratio specific surface area and true specific gravity of the obtained refined pitch covering black lead are combined with Table 1 and are shown. Since the measured value of quinoline soluble is 7.8% the covering ratio of this refined pitch

covering black lead is 0.078.

[0118] This refined pitch covering black lead was calcinated at 1000 °C among a nitrogen atmosphere for 1 hour (the heating rate of 25 °C / hr) and it carbonized. The specific surface area of this carbonization pitch covering black lead, true specific gravity, an R value and the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1 and are shown. As a result of particle-size-distribution measurement of this carbonization pitch covering black lead having distribution in 0.1-150 micrometers like a core material was checked and the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and carbonization pitch covering black lead. As a result of SEM observation the artificial graphite which is a core material was covered with the carbonization pitch which forms an enveloping layer and it was checked that the edge part is round.

[0119] The anode was produced using this carbonization pitch covering black lead and the nonaqueous secondary battery was produced using the propylene carbonate in which LiClO_4 of 1 mol/dm³ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2 and is shown.

[0120] The anode was produced using carbonization pitch covering black lead and subsequently the solid electrolyte lithium secondary battery was produced. The charge-and-discharge characteristic measurement result is combined with Table 3 and is shown.

Embodiment 14 -- a spherical meso-carbon-micro-beads graphitization article ("MCMB-6-28" by Osaka Gas Co. Ltd.) Diameter of centriole = 6.0 mm, particle size distribution = 0.1-50 micrometers, $d_{002} = 0.336 \text{ nm}$, $L_c = 50 \text{ nm}$, $L_a = 90 \text{ nm}$, specific surface area = $3.0 \text{ m}^2/\text{g}$, $R \text{ value} = 0.42$, true-specific-gravity = 2.20 g/cm^3 , 50g and the coal tar pitch of 80 °C of softening temperatures that removed primary QI beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 500-ml SEPARER flask, agitation mixing was carried out at 200 °C under ordinary pressure for 2 hours and the crude pitch covering meso-carbon-micro-beads graphitization article was obtained.

[0121] After adding one copy of toluene to one copy of obtained crude pitch covering meso-carbon-micro-beads graphitization article and carrying out washing processing at 80 °C under churning for 1 hour it filtered and the refined pitch covering meso-carbon-micro-beads graphitization article was obtained. It was 6.2 micrometers when the diameter D50 of a centriole of this refined pitch covering meso-carbon-micro-beads graphitization article was measured. Since the diameter D50 of a centriole of black lead as a core material was 6.0 micrometers the thickness of a pitch layer is 0.1 micrometer.

[0122] The covering ratio, specific surface area and true specific gravity of this refined pitch covering meso-carbon-micro-beads graphitization article are shown in Table 1. Since the value of quinoline soluble is 9.8% a covering ratio is 0.098.

[0123] This refined pitch covering meso-carbon-micro-beads graphitization article was calcinated at 1000 °C among a nitrogen atmosphere for 1 hour (the heating rate of 25 °C / hr) and it carbonized. The specific surface area of this carbonization pitch covering meso-carbon-micro-beads graphitization article, true specific gravity, an R value and the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1 and are shown. Having distribution in 0.1-50 micrometers like a core material was

checked as a result of particle-size-distribution measurement of this carbonization pitch covering meso-carbon-micro-beads graphitization article. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and a carbonization pitch covering meso-carbon-micro-beads graphitization article.

[0124]The anode was produced using this carbonization pitch covering meso-carbon-micro-beads graphitization article and the nonaqueous secondary battery was produced using the propylene carbonate in which LiClO_4 of 1 mol dm^{-3} was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is shown in Table 2.

An embodiment 15 massive artificial graphite (diameter Dof centriole $50=16.2 \mu\text{m}$ and $0.1\text{--}120 \mu\text{m}$ micrometers of particle size distribution) $d_{002}=0.337 \text{ nm}$ $L_c=100 \text{ nm}$ $L_a=71 \text{ nm}$ specific surface area $=14.4 \text{ m}^2/\text{g}$ $R \text{ value}=0.31$ the true specific gravity of 1.96 g/cm^3 50g and the coal tar pitch of 80 ** of softening temperatures that removed primary Q1 beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 1000-ml SEPARERU flask agitation mixing was carried out by 250 ** ordinary pressure for 5 hours and crude pitch covering black lead was obtained.

[0125]After adding three copies of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 50 ** under churning for 5 hours it filtered and refined pitch covering black lead was obtained. It was 16.6 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of black lead as a core material was 16.2 micrometers the thickness of a pitch layer is 0.2 micrometer.

[0126]The covering ratio of the obtained refined pitch covering black lead specific surface area and true specific gravity are shown in Table 1. Since the measured value of quinoline soluble is 11.3% the covering ratio of the carbon material for covering formation is 0.113.

[0127]This refined pitch covering black lead was calcinated at 1000 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr) and it carbonized. The specific surface area of the obtained carbonization pitch covering black lead true specific gravity and γ value and the volume reference integrated value of a particle of 1 micrometer or less are shown in Table 1. As a result of particle-size-distribution measurement it has distribution in $0.1\text{--}120 \mu\text{m}$ micrometers and the X diffraction measurement result was the same as that of a core material. By comparison of the R value of a core material and carbonization pitch covering black lead the carbonization pitch which is a carbon material for covering formation was understood that a degree of crystallinity is lower than a core material. As a result of SEM observation the artificial graphite of the core material was covered with the carbonization pitch which is a carbon material for covering formation and it was checked that the edge part is round.

[0128]This carbonization pitch covering black lead was used the anode was produced and the nonaqueous secondary battery was produced using the propylene carbonate in which LiClO_4 of 1 mol dm^{-3} was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is shown in Table 2.

An embodiment 16 massive artificial graphite (diameter Dof centriole $50=16.2 \mu\text{m}$ and $1\text{--}80 \mu\text{m}$ micrometers of particle size distribution) $d_{002}=0.338 \text{ nm}$ $L_c=83 \text{ nm}$ $L_a=63 \text{ nm}$ specific surface area $=6.8 \text{ m}^2/\text{g}$ $R \text{ value}=0.38$ the true specific gravity of 2.02 g/cm^3 50g and the coal tar pitch of 80 ** of softening temperatures that removed primary Q1

beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 1000-ml SEPARERU flask agitation mixing was carried out by 250 ** ordinary pressure for 5 hours and crude pitch covering black lead was obtained. After adding three copies of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 50 ** under churning for 5 hours it filtered and refined pitch covering black lead was obtained. It was 12.0 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of black lead as a core material was 11.6 micrometers the thickness of a pitch layer is 0.2 micrometer.

[0129] The covering ratio of the obtained refined pitch covering black lead specific surface area and true specific gravity are shown in Table 1. Since the measured value of quinoline soluble is 12.3% a covering ratio is 0.123.

[0130] This refined pitch covering black lead was calcinated at 1000 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr) and it carbonized. The specific surface area of the obtained carbonization pitch covering black lead true specific gravitan R value and the volume reference integrated value of a particle of 1 micrometer or less are shown in Table 1. As a result of particle-size-distribution measurement it has distribution in 1-80 micrometers and the X diffraction measurement result was the same as that of a core material. By comparison of the R value of a core material and carbonization pitch covering black lead the carbonization pitch which is a carbon material for covering formation was understood that a degree of crystallinity is lower than a core material. As a result of SEM observation the artificial graphite of the core material was covered with the carbonization pitch which is a carbon material for covering formation and it was checked that the edge part is round.

[0131] This carbonization pitch covering black lead was used the anode was produced and the nonaqueous secondary battery was produced using the propylene carbonate in which LiClO_4 of 1 mol dm^{-3} was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is shown in Table 2.

Embodiment 17 scale-like artificial graphite (diameter Dof centriole 50=18.9 micrometer and 0.1-150 micrometers of particle size distribution) $d_{002}=0.340 \text{ nm}$ $L_c=42 \text{ nm}$ $L_a=50 \text{ nm}$ specific surface area = $9.2 \text{ m}^2/\text{g}$ R value = 0.49 the true specific gravity of $1.82 \text{ g}/\text{cm}^3$ 50g and the coal tar pitch of 80 ** of softening temperatures that removed primary QI beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 1000-ml SEPARERU flask agitation mixing was carried out by 250 ** ordinary pressure for 5 hours and crude pitch covering black lead was obtained. After adding three copies of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 50 ** under churning for 5 hours it filtered and refined pitch covering black lead was obtained. It was 19.3 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of black lead as a core material was 18.9 micrometers the thickness of a pitch layer is 0.2 micrometer.

[0132] The covering ratio of the obtained refined pitch covering black lead specific surface area and true specific gravity are shown in Table 1. Since the measured value of quinoline soluble is 10.6% a covering ratio is 0.106.

[0133] This refined pitch covering black lead was calcinated at 1000 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr) and it carbonized. The specific

surface area of the obtained carbonization pitch covering black lead true specific gravity and the volume reference integrated value of a particle of 1 micrometer or less are shown in Table 1. As a result of particle-size-distribution measurement it has distribution in 0.1-150 micrometers and the X diffraction measurement result was the same as that of a core material. By comparison of the R value of a core material and carbonization pitch covering black lead the carbonization pitch which is a carbon material for covering formation was understood that a degree of crystallinity is lower than a core material. As a result of SEM observation the artificial graphite of the core material was covered with the carbonization pitch which is a carbon material for covering formation and it was checked that the edge part is round.

[0134] This carbonization pitch covering black lead was used the anode was produced and the nonaqueous secondary battery was produced using the propylene carbonate in which LiClO_4 of 1 mol/dm³ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is shown in Table 2.

the artificial graphite (the diameter D of a centriole -- 50 = 23.8 micrometers) of embodiment 18 whisker shape 0.1-150 micrometers of particle-size-distribution d 002 = 0.347 nm Lc = 25 nm La = 15 nm specific surface area = 13.5 m²/g R value = 0.68 true-specific-gravity 1.60 g/cm³ 50g and the coal tar pitch of 80 ** of softening temperatures which removed primary QI beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 1000-ml SEPARERU flask agitation mixing was carried out by 250 ** ordinary pressure for 5 hours and crude pitch covering black lead was obtained. After adding three copies of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 50 ** under churning for 5 hours it filtered and refined pitch covering black lead was obtained. It was 24.2 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of black lead as a core material was 23.8 micrometers the thickness of a pitch layer is 0.2 micrometer.